#### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : Confirmation No. 4337

Keiichi KONDO et al. : Attorney Docket No. 2006 0699A

Serial No. 10/580,472 : Group Art Unit 2831

Filed May 24, 2006 : Examiner Eric W. Thomas

ELECTRIC DOUBLE-LAYER CAPACITOR, ITS MANUFACTURING METHOD, AND

ELECTRONIC DEVICE USING SAME : Mail Stop: AMENDMENT

# SUBMISSION OF VERIFIED ENGLISH TRANSLATIONS OF PRIORITY APPLICATIONS

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

Sir:

Submitted herewith are English translations of the Japanese priority applications (JP 2004-010093 and JP 2004-017883) on which foreign priority is claimed in the present application. These English translations are accompanied by a "Verification of a Translation" verifying that the English translations are true and complete translations of these Japanese applications.

Respectfully submitted,

Keiichi KONDO et al.

/Charles R Watts/

By: 2008.04.15 11:11:58 -04'00'

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#### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Keiichi KONDO et al.

: Art Unit:

Serial No.: 10/580,472

: Examiner:

Filed: May 24, 2006

FOR:

ELECTRIC

DOUBLE-LAYER

CAPACITOR,

ITS

MANUFACTURING METHOD, AND ELECTRONIC DEVICE USING

**SAME** 

## **VERIFICATION OF A TRANSLATION**

Assistant Commissioner for Patents Washington, D.C. 20231 SIR:

I, the below named translator, hereby declare that:

- 1. My name and post office address are as stated below.
- 2. That I am knowledgeable in the English language and in the language of JP2004-010093 and JP2004-017883, and I believe the attached English translation to be a true and complete translation of JP2004-010093 and JP2004-017883.
- 3. The document for which the attached English translation is being submitted is a patent application on an invention entitled ELECTRIC DOUBLE-LAYER CAPACITOR, ITS MANUFACTURING METHOD, AND ELECTRONIC DEVICE USING SAME.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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#### [REPRESENTATION OF FEE]

[NUMBER IN LEDGER OF IN-ADVANCE PAYMENT] 011305 [AMOUNT] 21,000 yen

## [LIST OF ARTICLES FILED]

[NAME OF ARTICLE] Scope of Claims 1

[NAME OF ARTICLE] Specification 1

[NAME OF ARTICLE] Drawing 1

[NAME OF ARTICLE] Abstract 1

[NUMBER OF GENERAL POWER OF ATTORNEY] 9809938

## [Name of the Document]

Claims

## [Claim 1]

An electric double-layer capacitor comprising a case, an electrolytic solution filled in the case, and at least two sheets of electrode foil immersed in the electrolytic solution, wherein at least one sheet of the two electrode foil sheets is made of aluminum, and at least one surface of the front and back surfaces thereof is covered with aluminum fluoride.

#### [Claim 2]

The electric double-layer capacitor of claim 1, wherein active carbon is affixed to a surface covered with aluminum fluoride of the electrode foil, and at least some hydrophilic group of the active carbon is substituted by fluorine.

#### [Claim 3]

A method for manufacturing an electric double-layer capacitor comprising a case, an electrolytic solution filled in the case, and at least two sheets of electrode foil immersed in the electrolytic solution, wherein at least one sheet of the two electrode foil sheets is made of aluminum, and at least one surface of the front and back surfaces thereof is covered with aluminum fluoride, wherein at least one surface of the front and back surfaces of the electrode foil made of aluminum is covered with aluminum fluoride by using a plasma treatment method.

#### [Claim 4]

The method for manufacturing an electric double-layer capacitor of claim 3, wherein the front and back surfaces of the electrode foil are simultaneously covered with aluminum fluoride.

## [Claim 5]

An electronic device wherein the electric double-layer capacitor of claim 1 is connected to a power supply line of a motor.

#### [Claim 6]

The electronic device of claim 5, wherein a plurality of the electric double-layer capacitors of claim 1 are connected to the power supply line of the motor in a series or parallel fashion.

## [Claim 7]

An electronic device wherein the electric double-layer capacitor of claim 1 is connected to a power supply line between a motor and a fuel cell.

[Claim 8]

The electronic device of claim 7, wherein a plurality of series-connection bodies are connected to the power supply line between the motor and the fuel cell.

[Name of the Document] Specification

[Title of the Invention] Electric double-layer capacitor and its manufacturing method, and electronic device using the same

[Field of the Invention]

[0001]

The present invention relates to an electric double-layer capacitor and its manufacturing method, and an electronic device using the same.

[Background Art]

[0002]

Conventionally, an electric double-layer capacitor comprises a case, an electrolytic solution filled in the case, and at least two sheets of electrode foil made of aluminum immersed in the electrolytic solution. The electric double-layer capacitor is large in electrostatic capacitor, enabling the application of a high electrical current, and its use in electronic devices of electric motorcars for example is positively examined.

[0003]

As prior technical document information about the invention of this application, for example, Patent document 1 is commonly known.

[Patent document 1] Unexamined Japanese Patent Publication H10-271611.

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0004]

This type of electric double-layer capacitor cannot be increased in withstand voltage, and therefore, when it is used as a power supply unit in an electric motorcar for example, it is required to connect a large-capacity electric double-layer capacitor in a series fashion. For example, when the withstand voltage of the electric double-layer capacitor is 2V and the required voltage is 400V, it is necessary to use 200 pieces of electric double-layer capacitors. As a result, the power supply unit becomes very large in size. That is, if the withstand voltage of each electric double-layer capacitor can be increased, it will become possible to reduce the size of the power supply unit.

## [0005]

On the other hand, it is also examined to enhance the withstand voltage of electrolytic solution, and an electrolytic solution being relatively high in withstand voltage is developed.

## [0006]

As a cause of being low in withstand voltage of an electric double-layer capacitor, deterioration of electrode foil made of aluminum can be mentioned. In this case, even when an electrolytic solution being relatively high in withstand voltage, there arises a problem that the electric double-layer capacitor becomes lowered in withstand voltage.

## [0007]

The object of the present invention is to enhance the withstand voltage of an electric double-layer capacitor by preventing deterioration of the electrode foil.

[Means to Solve the Problems]

#### [8000]

In order to achieve the purpose, the invention of claim 1 is especially

configured in that at least one surface of the front and back surfaces of electrode foil made of aluminum is covered with aluminum fluoride, by which the deterioration of the electrode foil can be prevented. That is, since aluminum fluoride is very strong in bonding of fluorine atom and aluminum atom, aluminum elution into the electrolytic solution with voltage supplied can be suppressed. As a result, it is possible to prevent the electrode foil from deterioration.

## [0009]

The invention of claim 2 is configured in that active carbon is affixed to the surface of electrode foil covered with aluminum fluoride, and at least some hydrophilic group of the active carbon is substituted by fluorine. In addition to the same advantage as in claim 1, the permeability of the electrolytic solution to the electrode foil is improved, enhancing the actual surface area of the electrode foil, and as a result, it is possible to enhance the electrostatic capacity. That is, since at least a part of the active carbon is substituted by hydrophobic fluorine, the affinity between the active carbon and the hydrophobic electrolytic solution is improved, and it becomes easier for the electrolytic solution to penetrate into the pores of the electrode foil. Accordingly, it brings about such an advantage that the electrostatic capacity can be enhanced by enhancing the actual surface area of the electrode.

## [0010]

The invention of claim 3 is configured in that the surface of the electrode foil made of aluminum is covered with aluminum fluoride by using a plasma treatment method. It brings about such an advantage that the

electrode foil surface can be easily and uniformly covered with aluminum fluoride.

#### [0011]

Also, performing a dry process of plasma treatment, for example, the problem of electrostatic capacity lowering that takes place in a wet process using hydrogen fluoride or the like can be solved. That is, when electrode foil with active carbon affixed thereto by a wet process is treated, aluminum fluoride then produced will also stick to the active carbon, causing the actual electrode surface area to be decreased, and consequently, there arises a problem of lowering of the electrostatic capacity, but such a problem will not occur in a dry process.

## [0012]

The invention of claim 4 is configured in that the front and back surfaces of electrode foil are simultaneously covered with aluminum fluoride. In this way, since aluminum fluoride is formed on the front and back surfaces of electrode foil at one time, it brings about such an advantage that the productivity can be enhanced.

#### [0013]

The invention of claim 5 is configured in that the electric double-layer capacitor of claim 1 is connected to the power supply line of a motor, and the required number of capacitors can be reduced because the electric double-layer capacitor used is increased in withstand voltage. As a result, it brings about such an advantage that the electronic device can be reduced in size.

#### [0014]

The invention of claim 6 is configured in that a plurality of the electric double-layer capacitors of claim 1 are connected to the power supply line of a motor in a series or parallel fashion, and it brings about the same advantage as in claim 5.

[0015]

The invention of claim 7 is configured in that the electric double-layer capacitor of claim 1 is connected to the power supply line between a motor and fuel cell. Accordingly, it brings about such an advantage that the electric double-layer capacitor assists the fuel cell for power supply to the motor in the initial drive of the motor.

[0016]

The invention of claim 8 is configured in that a plurality of the electric double-layer capacitors of claim 1 are connected to the power supply line between a motor and fuel cell. And, it brings about the same advantage as in claim 7.

[Advantages of the Invention]

[0017]

The present invention is especially configured in that at least one surface of the front and back surfaces of electrode foil made of aluminum is covered with aluminum fluoride, and thereby, the deterioration of the electrode foil can be prevented. That is, since aluminum fluoride is very strong in bonding of fluorine atom and aluminum atom, aluminum elution into the electrolytic solution with voltage supplied can be suppressed. As a result, it is possible to prevent the electrode foil from deterioration.

[Detailed Description of the Preferred Embodiments]

## [0018]

The electric double-layer capacitor and its manufacturing method of the present invention, and an electronic device using the same will be described in the following with reference to one preferred embodiment and the drawings. An electric motorcar is used as the electronic device. [0019]

Fig. 1 is a partially broken perspective view of a electric double-layer capacitor in one preferred embodiment. Fig. 2 is a perspective view of the electric double-layer capacitor. In Fig. 1 and Fig. 2, the electric double-layer capacitor comprises aluminum case 1 (container), electrolytic solution 2 filled in aluminum case 1, and two sheets of electrode foil 3 made of aluminum which is immersed in electrolytic solution 2. Electrode foil 3 and separator 4 are alternately put and wound on each other in a suspended fashion as shown in Fig. 1. Also, lead wire 3A made of aluminum is connected to each of the two sheets of electrode foil 3, and lead wire 3A is led out of aluminum case 1 through sealing rubber 3B. Also, the front and back surfaces of electrode foil 3 made of aluminum are covered with aluminum fluoride 5 and active carbon 6 as shown in Fig. 5.

[0020]

The operational principle of the electric double-layer capacitor is described in the following. Fig. 3 illustrates the principle of operation of the electric double-layer capacitor. Fig. 3 (a) and Fig. 3 (b) are sectional views of the electric double-layer capacitor in a state of charge and a state of discharge respectively. In Fig. 3 (a), during the charge, anion 9 in electrolytic solution 2 is drawn closer to active carbon 7 of the anode, and

cation 10 is drawn closer to active carbon 8 of the cathode, respectively by electrostatic attraction, then an ionic layer called an electric double-layer is formed near each of active carbon 7 of the anode and active carbon 8 of the cathode, and electric charge is accumulated. On the other hand, in Fig. 3 (b), due to the discharge, anion 9 and cation 10 are released from active carbon 7 of the anode and active carbon 8 of the cathode, which are then diffused in electrolytic solution 2.

#### [0021]

The electric double-layer capacitor of the present invention is characterized in that the surface of electrode foil 3 is covered with aluminum fluoride 5 as shown in Fig. 5. Conventionally, the electrode of an electric double-layer capacitor uses aluminum covered with active carbon, and as shown in Fig. 3 (a), the electrode is deteriorated due to elution of the aluminum with voltage supplied. The following can be considered as a cause of this phenomenon. That is, the surface of aluminum usually has oxide film or aluminum oxide, and weak bonding between aluminum atom and oxygen atom must be the cause of the phenomenon. On the other hand, in the case of aluminum fluoride, the bonding of aluminum atom and fluorine atom is stronger as compared with the bonding between aluminum atom and oxygen atom, and therefore, it can be considered that it is possible to suppress the elution of aluminum into electrolytic solution 2.

#### [0022]

As a method of forming such aluminum fluoride, a plasma treatment method can be mentioned. Fig. 4 (a) shows a sectional view of a of plasma treatment process. Fig. 4 (a) is a sectional view of a plasma treatment chamber, and Fig. 4 (b) is a sectional view of a plasma generation chamber. Plasma treatment chamber 17 and plasma generation chamber 18 are connected to each other via chamber connection hole 19. In Fig. 4 (b), a mixed gas of argon and carbon tetrafluoride is applied between electrodes 18B, 18C connected to high frequency power source 18A from gas inlet hole 11, and thereby, plasma is generated, and the plasma is supplied from outlet hole 12 to plasma treatment chamber 17 via plasma inlet hole 13. [0023]

In Fig. 4 (a), plasma is introduced into plasma treatment chamber 17 from plasma inlet hole 13. In plasma treatment chamber 17 is prepared electrode foil 16 in the form of a roll. Electrode foil 16 delivered from the electrode foil unwinding side as untreated electrode foil 14 is taken up as treated electrode foil 15 at the electrode foil winding side after the plasma treatment. In this way, since the front and back surfaces of electrode foil 16 are simultaneously treated by plasma, the productivity can be enhanced as compared with the case of performing separate treatment. Electrode foil 16 shown in Fig. 4 is cut to a proper length and used as electrode foil 3 shown in Fig. 1.

#### [0024]

When plasma treatment is performed before affixing active carbon 6 shown in Fig. 5 to electrode foil 16 shown in Fig. 4, it results in that aluminum fluoride 5 existing between electrode foil 3 made of aluminum and active carbon 6 shown in Fig. 5 causes the electrode to become high in resistance value. Accordingly, it is desirable to perform the plasma treatment after affixing active carbon 6 to electrode foil 3 as shown in Fig. 5.

## [0025]

Fig. 5 is a sectional view of electrode foil 3 plasma-treated after affixing active carbon 6 to the front and back surfaces of electrode foil 3. A mixture of active carbon 6, conductive assistant 21, and binder 22 is used for the purpose of affixing active carbon 6 to electrode foil 3, and the mixing ratios are respectively 80, 10, 10 by weight. Active carbon 6, as shown in Fig. 5 (b), has a hydrophilic group such as hydroxyl group and carboxyl group at the end thereof, and is lower in affinity with hydrophobic electrolytic solution. That is, it can be said that the wettability is poor in the electrolytic solution.

## [0026]

However, since the hydrophilic group is substituted by fluorine as a result of plasma treatment, it is possible to improve the poor wettability. That is, the affinity between active carbon 6 and hydrophobic electrolytic solution 2 is enhanced, and electrolytic solution 2 becomes easier to penetrate into the pores of electrode foil 3. In this way, the actual electrode surface area is increased and it brings about such an advantage that the electrostatic capacity can be enhanced.

## [0027]

Fig. 6 shows a withstand voltage characteristic chart in the anode of the electric double-layer capacitor in the present preferred embodiment. Here, the potential in current value 0.01mA is defined as the withstand voltage of anode. Also, tetrafluoroboric acid tetraethylammonium is used as electrolytic solution 2.

#### [0028]

In case the plasma treatment of fluorine is not performed, that is, the withstand voltage of conventional electrode foil is 0.9V (A in Fig. 6), while the withstand voltage of electrode foil 3 after plasma treatment is 1.5V (B in Fig. 6). In the comparison of withstand voltages with respect to electric double-layer capacitors, the withstand voltage of conventional electric double-layer capacitor is 2.0V, while the withstand voltage of electric double-layer capacitor of the present invention is 2.6V. That is, it can be said that the withstand voltage has been enhanced by 30%.

As described above, by using electrode foil 3 whose surface is covered with aluminum fluoride 5, it is possible to enhance the withstand voltage of the electric double-layer capacitor.

## [0030]

[0029]

Fig. 7 is a system flowchart of an electric motorcar in the present preferred embodiment, and Fig. 8 is a circuit diagram of the interior of a capacitor unit. The electric motorcar comprises motor 31 connected to axle 31A, fuel cell 32 for supplying power to motor 31, and capacitor unit 33 connected to the power supply line. Capacitor unit 33 includes a plurality of series connected electric double layer capacitors of the present invention shown in Fig. 1 and Fig. 2. In Fig. 7, reference numeral 32A is hydrogen tank, numeral 32B is humidifier, numeral 32C is water tank, numeral 33D is air compressor, and numeral 33E is motor controller. Arrow mark A is the flow of hydrogen, arrow mark B is the flow of water, and arrow mark C is the flow of air. Reference numeral 33A of Fig. 8 is charge/discharge control circuit. In Fig. 8, the required voltage of capacitor unit 33 is 400V.

In the case of using conventional electric double-layer capacitors, it is necessary to use 200 capacitors, while when using the electric double-layer capacitors of the present invention, it is just enough to use 151 capacitors because the withstand voltage is 2.6V as described above. That is, the size of capacitor unit 33 can be reduced, and as a result, the electronic device can be reduced in size. Incidentally, it is possible to connect a plurality of the electric double-layer capacitors to the power supply line of motor 31 in a parallel or series fashion as needed.

[0031]

Also, in the present preferred embodiment, an electric motorcar is used as the electronic device, but the invention is not limited to this.

[Industrial Applicability]

[0032]

The electric double-layer capacitor of the present invention brings about such an advantage that deterioration of the electrode foil can be prevented, which is therefore useful for power sources of various electronic devices.

[Brief Description of the Drawings]

[0033]

Fig. 1 is a partially broken perspective view of an electric double-layer capacitor in one preferred embodiment.

Fig. 2 is a perspective view of the electric double-layer capacitor.

Fig. 3 (a) and (b) are sectional views showing the operational principle of the electric double-layer capacitor respectively in a state of charge and in a state of discharge.

Fig. 4 (a) and (b) are sectional views showing the manufacturing process in the preferred embodiment.

Fig. 5 is a sectional view of electrode foil in the preferred embodiment.

Fig. 6 is a withstand voltage characteristic of anode of the electric double-layer capacitor in the preferred embodiment.

Fig. 7 is a system flowchart of an electronic device in the preferred embodiment.

Fig. 8 is a circuit diagram of an essential portion of the device.

## [Description of the Reference Numerals and Signs]

#### [0034]

-	4.7	
	Aluminum	case

- 2 Electrolytic solution
- 3 Electrode foil made of aluminum
- 4 Separator
- 5 Aluminum fluoride
- 6 Active carbon
- 7 Active carbon of anode
- 8 Active carbon of cathode
- 9 Anion
- 10 Cation
- 11 Gas inlet hole
- 12 Plasma outlet hole
- 13 Plasma inlet hole
- 14 Untreated electrode foil

Treated electrode foil **1**5 17 Plasma treatment chamber 18 Plasma generation chamber 19 Chamber connecting hole 21 Conductive assistant 22 Binder 31 Motor 32 Fuel cell Capacitor unit 33

[Name of the Document]

Abstract

[Abstract]

[Object] The object of the present invention is to enhance the withstand voltage of the electric double-layer capacitor by preventing deterioration of the electrode foil.

[Means to Solve the Problems] In order to achieve the purpose, the present invention comprises case 1, electrolytic solution 2 filled in case 1, and at least two sheets of electrode foil 3 immersed in electrolytic solution 2, wherein at least one of the two sheets of electrode foil 3 is made of aluminum, and at least one of the front and back surfaces thereof is covered with aluminum fluoride 5, and thereby, it is possible to prevent deterioration of the electrode foil.

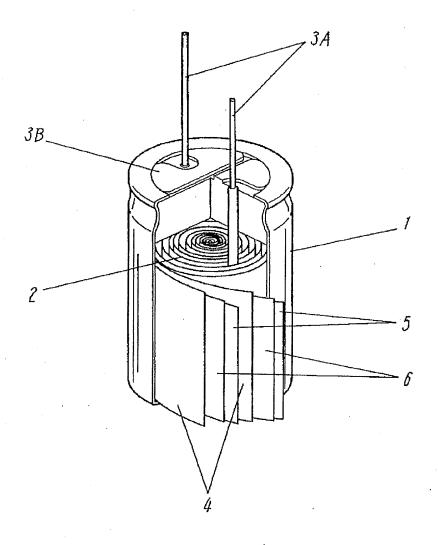
[Selected Drawing] Fig. 1

## [Name of the Document]

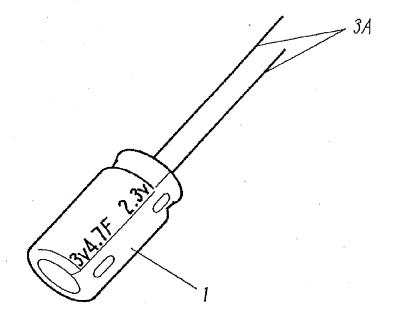
## Drawing

[Fig. 1]

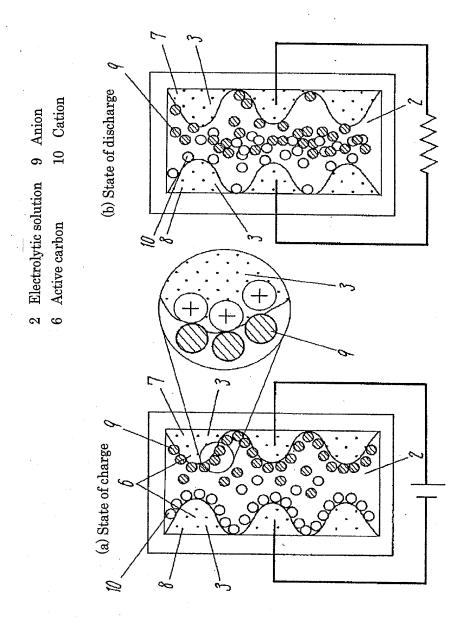
- 1 Aluminum case
- 2 Electrolytic solution
- 3 Electrode foil made of aluminum
- 4 Separator
- 5 Aluminum fluoride
- 6 Active carbon



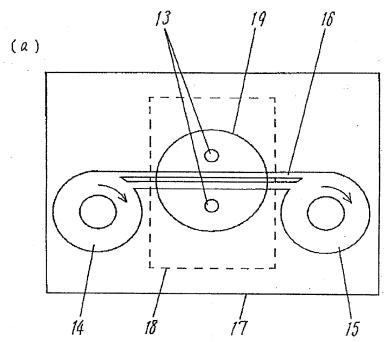
[Fig. 2]



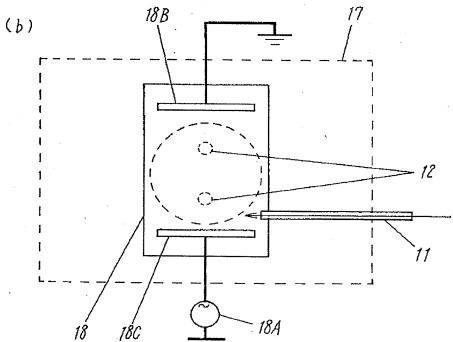
[Fig. 3]



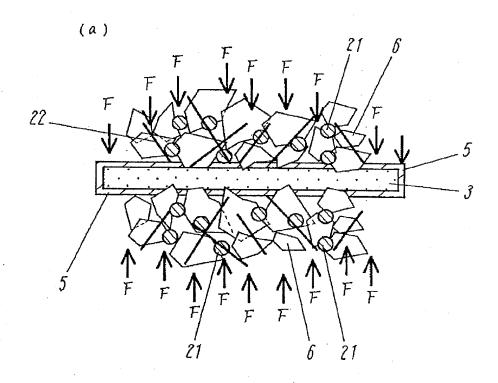
[Fig. 4]

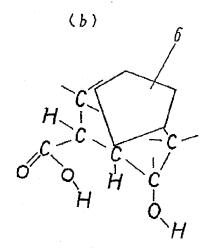


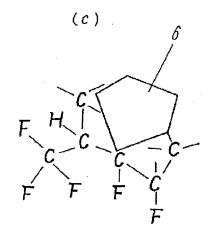
- 11 Gas inlet hole
- 13 Plasma inlet hole
- 16 Electrode foil
- 17 Plasma treatment chamber
- 18 Plasma generation chamber
- 18A High frequency power source
- 19 Chamber connecting hole



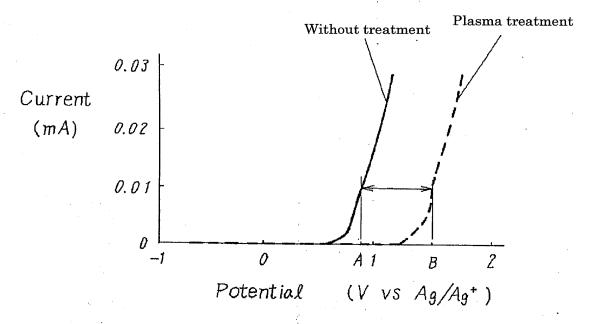
- 6 Active carbon
- 21 Conductive assistant
- 22 Binder



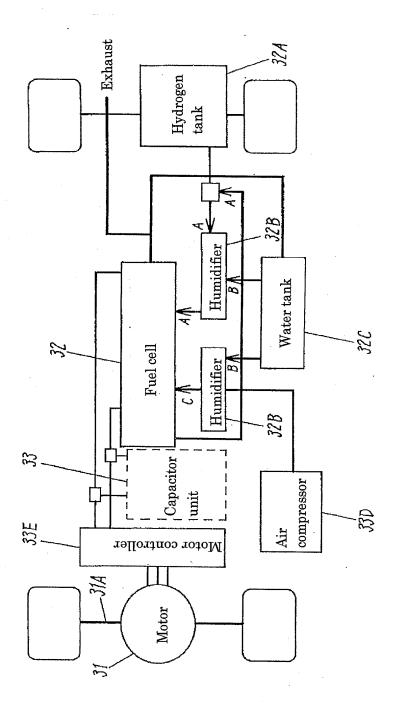




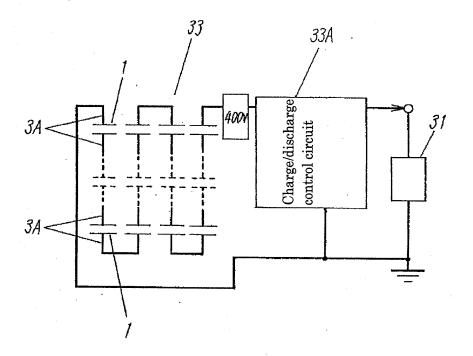
[Fig. 6]



[Fig. 7]



[Fig. 8]



[NAME OF THE DOCUMENT] Patent Application

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[DATE OF FILING] January 27, 2004

[ADDRESS] Director-General of the Patent Office

[INTERNATIONAL PATENT CLASSIFICATION] H01G 9/016

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[REPRESENTATION OF FEE]

[NUMBER IN LEDGER OF IN-ADVANCE PAYMENT] 011305

[AMOUNT] 21,000 yen

[LIST OF ARTICLES FILED]

[NAME OF ARTICLE] Scope of Claims 1

[NAME OF ARTICLE] Specification 1

[NAME OF ARTICLE] Drawing 1

[NAME OF ARTICLE] Abstract 1 [NUMBER OF GENERAL POWER OF ATTORNEY] 9809938

## [Name of the Document]

Claims

#### [Claim 1]

An electric double-layer capacitor comprising an element with a pair of polarizing electrodes wound thereon having a separator therebetween, or an element with a pair of polarizing electrodes laminated thereon having a separator therebetween, which is inserted and sealed in a case together with an electrolytic solution, wherein a material containing an alloy of carbon and aluminum is used for the electrodes.

#### [Claim 2]

The electric double-layer capacitor of claim 1, wherein the ratio of carbon to aluminum of the alloy formed from carbon and aluminum is 3:4.

[Claim 3]

A method of manufacturing an electrode for an electric double-layer capacitor wherein an alloy of carbon and aluminum is formed by applying carbon onto aluminum foil and heating it to above the alloying temperature of both.

#### [Claim 4]

A method of manufacturing an electrode for an electric double-layer capacitor wherein an alloy of carbon and aluminum is formed by forming carbon on aluminum foil by using a vacuum evaporation method, sputtering method or CVD method and heating it to above the alloying temperature of both.

#### [Claim 5]

A method of manufacturing an electrode for an electric double-layer capacitor wherein an alloy of carbon and aluminum is formed by forming aluminum on carbon foil by using a vacuum evaporation method, sputtering method or CVD method and heating it to above the alloying temperature of both.

[Name of the Document] Specification

[Title of the Invention] Electric double-layer capacitor and method of manufacturing electrode used for the same

[Field of the Invention]

[0001]

The present invention relates to an electric double-layer capacitor used in various electronic devices, and a method of manufacturing an electrode used for the same.

[Background Art]

[0002]

Conventionally, with respect to an electrode metal material used in contact with an electrolytic solution of an electric double-layer capacitor or the like and a capacitor using the material, a method of providing an electrode metal material capable of lowering the internal resistance is disclosed in Patent document 1 and Patent document 2. As disclosed in the documents, a method of lowering the internal resistance of an electrode by fixing carbon particles on valve metal such as aluminum to compensate for conduction between aluminum and electrode active carbon is commonly known.

[60003]

Also, as disclosed in Patent document 3, a method of forming a conductive layer by fully covering a collector having irregular surfaces with carbon black particles to lower the internal resistance of the electric double-layer capacitor is commonly known.

[0004]

In the technology mentioned in the open patent publication, all the collector and electrode are formed of simplex aluminum and carbon.

[0005]

On the other hand, mentioned in Patent document 1 and Patent document 2 is that aluminum portions are covered with oxide film caused due to water of the electrolytic solution, and the oxide film forming potential can be detected from the reaction potential at the oxidation side measured by CV measurement (cyclic voltammetry) for example, and an example is shown in Fig. 4. In Fig. 4, the reference electrode used is Ag/Ag+ electrode, and the paired electrodes used are Pt. For the working electrode, an aluminum electrode and an aluminum electrode with carbon particles fixed thereon are used and compared. From the result, it has been found that the reaction potentials are nearly equal in the case of aluminum electrode and aluminum electrode with carbon particles fixed thereon, showing that oxide film is formed on aluminum of both electrodes.

[Patent document 1] Unexamined Japanese Patent Publication H11-28849.

[Patent document 2] Unexamined Japanese Patent Publication No.2001-297952.

[Patent document 3] Unexamined Japanese patent Publication No.2000-269095.

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0006]

However, in the above configuration, there arises a problem such

that in order to form an electrode it is necessary to perform a process of fixing carbon particles on aluminum and fixing a half of carbon particles on aluminum by etching the aluminum to make the carbon particles slightly protruded, which is complicated and difficult to control.

## [0007]

Also, since only carbon particle is expected to compensate for conduction, an excessive burden is imposed on the reliability of fixing carbon particles, and also, the aluminum portion is covered with oxide film caused due to water of the electrolytic solution, making no contribution to conduction, and it is intended to lower the resistance by completely separating the conductive portion and the non-conductive portion from each other on the electrode, and therefore, each of the conductive portion and the non-conductive portion is provided with two functions on one electrode, resulting in lessening of the allowance in the electrode manufacturing process.

#### [8000]

Further, since the aluminum portion is covered with oxide film caused due to water of the electrolytic solution, there arise many problems such that the size of potential window is limited due to reaction in forming the oxide film, causing the withstand voltage to be limited.

#### [0009]

The present invention is intended to solve such conventional problems, and the object of the invention is to provide an electric double-layer capacitor which is structurally simple and capable of lowering the internal resistance of the capacitor.

[0010]

Further, the object of the invention is to provide a method of manufacturing an electrode for the electric double-layer capacitor capable of enhancing the withstand voltage by changing the electrode reaction potential to noble potential.

[Means to Solve the Problems]

[0011]

In order to solve the above problems, the invention of claim 1 of the present invention comprises an element with a pair of polarizing electrodes wound thereon having a separator therebetween, or an element with a pair of polarizing electrodes laminated thereon having a separator therebetween, which is inserted and sealed in a case together with an electrolytic solution, wherein a material containing an alloy of carbon and aluminum is used for the electrodes. Accordingly, the internal resistance of the capacitor can be lowered, and further, it is possible to efficiently enhance the withstand voltage by changing the reaction potential of the anode to noble potential. [0012]

The invention of claim 2 is the invention of claim 1, wherein the ratio of carbon to aluminum of the alloy of carbon and aluminum is 3:4. Accordingly, it is possible to most efficiently obtain the advantage obtained by the invention of claim 1.

[0013]

The invention of claim 3 is a method of manufacturing an electrode for electric double-layer capacitor, wherein an alloy of carbon and aluminum is formed by applying carbon onto aluminum foil and heating it to above the alloying temperature of both. In this way, it is possible to efficiently obtain an alloy of carbon and aluminum.

#### [0014]

The invention of claim 4 is a method of manufacturing an electrode for electric double-layer capacitor, wherein an alloy of carbon and aluminum is formed by forming carbon on aluminum foil by using a vacuum evaporation method, sputtering method or CVD method and heating it to above the alloying temperature of both. In this way, it is possible to efficiently form an alloy of carbon and aluminum.

#### [0015]

The invention of claim 5 is a method of manufacturing an electrode for electric double-layer capacitor, wherein an alloy of carbon and aluminum is formed by forming aluminum on carbon foil by using a vacuum evaporation method, sputtering method or CVD method and heating it to above the alloying temperature of both. In this way, it is possible to efficiently form an alloy of carbon and aluminum.

## [Advantages of the Invention]

## [0016]

As described above, according to the present invention, a carbon layer is formed on an aluminum layer, or an aluminum layer is formed on a carbon layer, which is alloyed by heating to form an alloy layer of carbon and aluminum. The layer including the alloy layer is used as a collector of the electric double-layer capacitor, thereby lowering the internal resistance of the capacitor, and also, changing the reaction potential of anode to noble potential. In this way, it is possible to enhance the withstand voltage of

the capacitor.

[Detailed Description of the Preferred Embodiment]
[0017]

The inventions of claims 1 to 5 in particular of the present invention will be described in the following by using the preferred embodiment.

[0018]

Fig. 1 is a manufacturing flowchart showing a method of manufacturing an electrode for the electric double-layer capacitor in one preferred embodiment of the present invention. In Fig. 1, aluminum foil is first thrown in, and a carbon black material of  $0.3~\mu$  m average grain diameter is applied to the aluminum foil. Subsequently, the aluminum foil coated with the carbon black material is rolled in a state of being heated at a temperature higher than  $300^{\circ}$ C, and thereby, an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> which is formed of aluminum and carbon is formed. The thickness of the alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> is about 1  $\mu$  m in SIMS analysis. Also, the alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> includes a specific level of variation as against the stoichiometric composition, and the variation becomes remarkable at the aluminum/Al<sub>4</sub>C<sub>3</sub> interface.

[0019]

Next, a wound type electric double-layer capacitor shown in Fig. 2 is manufactured by using an aluminum electrode including an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> manufactured this way. Fig. 2 is a partially broken perspective view showing the configuration of a wound type electric double-layer capacitor. In Fig. 2, reference numeral 3 is an electrode, and

electrode 3 is configured by forming electrode layer 2 based active carbon on the front and back surfaces of collector 1 formed of aluminum electrode including the alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub>. Reference numeral 4 is a separator, numeral 5 is a lead wire, numeral 6 is a ring packing, numeral 7 is a sealing material, and numeral 8 is a case.

## [0020]

A method of manufacturing a wound type electric double-layer capacitor configured in this way will be described in the following. First, as described by using Fig. 1, collector 1 is manufactured, which is configured in that an alloy layer of 1  $\mu$  m in thickness having a composition of Al<sub>4</sub>C<sub>3</sub> is formed on the front and back surfaces of an aluminum foil of 30  $\mu$  m in thickness. Subsequently, the front and back surfaces of collector 1 are coated with an electrode solution applied by 85  $\mu$  m each time, which is prepared by kneading active carbon with 8.1wt% binder such as PTFE and 10.8 wt% conductive assistant such as acetylene black mixed and a proper amount of water contained therein, followed by making it uniform in grain diameter by using a pressure homogenizer, thereby forming electrode layer 2 to manufacture electrode 3 of 200  $\mu$  m in thickness. After that, electrode 3 is press-formed in order to increase the electrode density and strength, obtaining a thickness of 195  $\mu$  m after press-forming.

#### [0021]

Subsequently, a pair of lead wires 5 are connected to the positive and negative electrodes of electrode 3, and then separator 4 of 35  $\mu$  m in thickness formed from cellulose material is sandwiched and wound between the positive and negative electrodes, thereby obtaining an element of 10 mm

in diameter and 40 mm in width.

[0022]

After that, the element is inserted into case 8 of 12 mm in diameter and 48 mm in height under a dehumidified atmosphere together with propylene carbonate as solvent, tetraborate fluoride of tetraethylene ammonium as solute, and electrolytic solution of 0.69 mol/kg in concentration, which is sealed by sealing material 7, thereby manufacturing an electric double-layer capacitor of the present preferred embodiment. [0023]

electric double layer capacitor of the present preferred embodiment configured as described above and a conventional example as a comparative example are manufactured 10 pieces each. The average values of the measured results with respect to the capacity and internal resistance are shown in Table 1. The conventional example is manufactured on the basis of the technology mentioned in Unexamined Japanese Patent Publication H11-28849 and Unexamined Japanese Patent Publication 2001-297952. Also, in the measurement, constant voltage charging at 2.0V is performed after constant current charging at 1.0A, and after maintaining it for 6 min. and 20 sec., the capacity and internal resistance are calculated from the behavior of voltage between terminals in constant current discharging at 1.0A. The resistance is calculated from the initial IR drop in discharging at constant current.

[0024]

[Table 1]

n = 10

	Conventional	Invention
Capacity [F]	95.1	96.2
Resistance $[m \Omega]$	31.2	20.1

### [0025]

As is obvious in Table 1, the internal resistance of the electric double-layer capacitor in the present preferred embodiment using a collector containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> formed from aluminum and carbon is lowered to nearly 2/3 as compared with the internal resistance of an electric double-layer capacitor using a conventional collector, and then, both are nearly equal in capacity. From this fact, it is found that an electric double-layer capacitor of low resistance can be obtained by using a collector containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> formed from aluminum and carbon to configure the electric double-layer capacitor without excessive lowering of the capacitor.

#### [0026]

Also, CV measurement has been performed in order to check the reaction potential of the collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> formed from aluminum and carbon in the present preferred embodiment. The results are shown in Fig. 3. The reference electrode used is Ag/Ag+ electrode, and the opposed electrode used is Pt. For the working electrode, a collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub>, an aluminum electrode with aluminum electrode and carbon particles fixed thereon, and an aluminum electrode are used for the purpose of comparison. From the results, it is clear that the

reaction potential of the collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> is more enhanced in noble potential as compared with the aluminum electrode with aluminum electrode and carbon particles fixed thereon or the aluminum electrode. From this fact, it can be considered that the use of an electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub> as a collector more expands the potential window as compared with the conventional electrode and it results in enhancement of the withstand voltage of the electric double-layer capacitor using a collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub>.

[0027]

As described above, an electric double-layer capacitor configured by using a collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub>, which is lower in resistance and higher in withstand voltage as compared with the conventional electric double-layer capacitor, can be easily obtained in accordance with the present invention.

[0028]

In the present preferred embodiment, as a method of forming a collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub>, carbon is coated on aluminum foil and it is heated to form a collector electrode, but the present invention is not limited to this method. It is also preferable to form carbon on aluminum foil by using vacuum technology such as evaporation.

[0029]

Also, in the present preferred embodiment, as a method of forming a collector electrode containing an alloy layer having a composition of Al<sub>4</sub>C<sub>3</sub>,

carbon is coated on aluminum foil and it is heated to form a collector electrode, but the present invention is not limited to this method. It is also preferable to evaporate aluminum on a carbon electrode and heat it to form a collector electrode.

[Industrial Applicability]

[0030]

The electric double-layer capacitor and the method of manufacturing an electrode using the capacitor are capable of lowering the internal resistance of the capacitor and enhancing the withstand voltage of the capacitor, which are therefore useful for various electronic devices.

[Brief Description of the Drawings]

[0031]

Fig. 1 is a flowchart showing a method of manufacturing an electrode of an electric double-layer capacitor in one preferred embodiment of the present invention.

Fig. 2 is a partially broken perspective view showing the configuration of a wound type electric double-layer capacitor in the preferred embodiment.

Fig. 3 is a characteristic chart showing the reaction potential at the oxidation side of a collector electrode in the preferred embodiment.

Fig. 4 is a characteristic chart showing the reaction potential at the oxidation side of a conventional collector electrode.

[Description of the Reference Numerals and Signs] [0032]

1 Collector containing alloy layer having Al<sub>4</sub>C<sub>3</sub> composition

- 2 Electrode layer
- 3 Electrode
- 4 Separator
- 5 Lead wire
- 6 Ring packing
- 7 Sealing material
- 8 Case

[Name of the Document]

Abstract

[Abstract]

[Object] The invention is intended to solve such problems that a complicated and hard-to-control process is required to form the electrode and that the withstand voltage is limited, and the object is to provide an electric double-layer capacitor which is structurally simplified and capable of lowering the internal resistance of the capacitor and to enhance the withstand voltage, and a method of manufacturing an electrode using the capacitor.

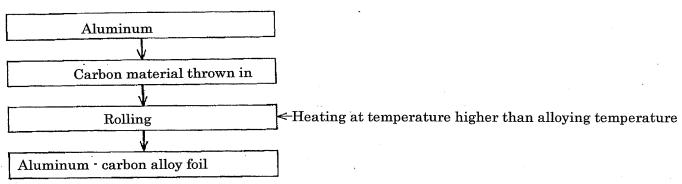
[Means to Solve the Problems] The electric double-layer capacitor uses a material containing an alloy formed from carbon and aluminum as a material for electrodes, and the electrode is manufactured by such a method that carbon is coated on aluminum foil and it is heated to a temperature above the alloying temperature of both in order to form an alloy of carbon and aluminum, and thereby, the internal resistance of the capacitor can be lowered, and further, it is possible to efficiently enhance the withstand voltage by changing the reaction potential of the anode to noble potential.

[Selected Drawing] Fig. 1

[Name of the Document]

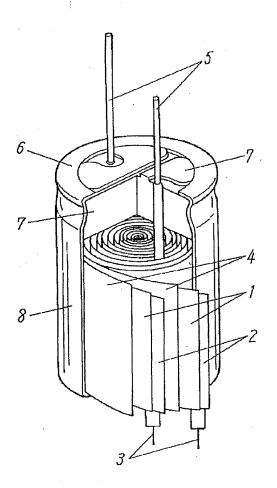
Drawings

[Fig. 1]

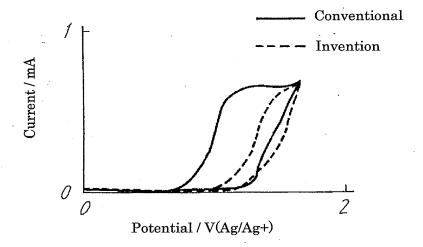


# [Fig. 2]

- 1 Collector formed with Al<sub>4</sub>C<sub>3</sub> layer
- 2 Electrode layer
- 3 Electrode
- 4 Separator
- 5 Lead wire
- 6 Ring packing
- 7 Sealing material
- 8 Case



[Fig. 3]



[Fig. 4]

